

# PATENT SPECIFICATION

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(19)

## (54) PROCESS FOR THE MANUFACTURE OF POLYCHLORO-POLYBROMO-COPPER PHTHALOCYANINES

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 5 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

10 The invention relates to a process for the manufacture of polychloro - polybromo - copper phthalocyanines.

15 Copper phthalocyanines polysubstituted by chlorine and bromine—hereinafter referred to as polychloro - bromo - copper phthalocyanines—are obtained conventionally (British Patents 925,266, 932,943 and 933,242) by passing chlorine into melts of aluminum chloride, sodium chloride and sodium bromide, containing copper phthalocyanine. 20 The chlorine is passed in until the desired hue or the desired ratio of chlorine to bromine in the halogeno - copper phthalocyanine is reached. These conventional processes suffer from various shortcomings, e.g. low space-time yields or inconsistent quality of the 25 halogenation products obtained from different batches. Thus, e.g., the chlorine introduced must be metered carefully to avoid major losses of bromine and this extends the time required for halogenation and lowers the 30 quality of the product. The conventional processes give halogenation products of very variable quality, in particular as regards the tinctorial strength, and therefore the products 35 are not equally suitable for all finishing processes, i.e. processes in which the crude pigment is converted into a valuable pigmentary form of high tinctorial strength.

40 Specifically, polyhalogeno - copper phthalocyanines of 14 to 16 halogen atoms which contain at least 7 bromine atoms are difficult to manufacture by the conventional processes. Thus, whilst the process described in British Patent Specification No. 925,266, examples I 45 to VI, gives polyhalogenated products, aliquot incorporation of bromine—present in the melt in the form of sodium bromide or potassium bromide—into the product is only possible

if the chlorine is introduced very slowly into the reaction mixture. As a result, industrial-scale batches demand very long reaction times. Thus, e.g., the halogenation according to example VI. of British Patent Specification No. 925,266, in which "parts" are to be interpreted as kilograms, requires at least 70 hours, contrary to the statements in the specification. The pigments obtained by these processes are very difficult, or even impossible, to finish by conventional processes (e.g. those of German Patent Specification No. 1,242,180 or U.S. Patent Specification No. 3,750,750). Further bromine atoms can only be incorporated into the phthalocyanine molecule by additional use of elementary bromine. Only then is a polychloro - bromo - copper phthalocyanine obtained which contains up to 67 per cent by weight of bromine, corresponding to 15 atoms of bromine per mole of copper phthalocyanine.

50 British Patent Specification No. 933,242 discloses that perhalogenation of copper phthalocyanine in an aluminum chloride/sodium bromide/sodium chloride melt is achievable not only with chlorine but also with other oxidizing agents. However, the degree of bromination of the copper phthalocyanine achievable by this process is less than that achievable by the process described in British Patent Specification No. 925,266. Furthermore, the process of British Patent Specification No. 933,242 again gives a polychloro - bromo - copper phthalocyanine of 55 variable composition.

55 According to British Patent Specification No. 932,943, the reproducibility and space-time yield are improved by using liquid bromine and mixtures of liquid or gaseous bromine and chlorine gas. This procedure 60 admittedly saves aluminum chloride but requires a greater excess of halogen, especially of bromine. As compared to the processes of British Patent Specifications Nos. 925,266 and 933,242, the data in example 3 (of British Patent Specification No. 932,943) show that an excess of 30% of bromine and of about 65 100% of chlorine is required, whilst accord-

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- ing to Example 1 an excess of as much as 100% of bromine is required.
- A serious disadvantage of the conventional processes is the instability of the starting compounds and of the partially halogenated starting compounds under the reaction conditions, above all at the start of the halogenation. As a result of this instability, a part of the copper in the copper phthalocyanine is replaced by aluminum so that a mixture of polyhalogenated copper phthalocyanine and aluminum phthalocyanine is obtained. Finished pigments prepared from these mixtures are substantially less deeply coloured and less economical in use, and less clear than those obtained from pure polyhalogeno - copper phthalocyanines. A further disadvantage of these polyhalogenated copper/aluminum phthalocyanine mixtures is that surface coatings coloured with the mixtures have poorer fastness to weathering than those coloured with pure polyhalogeno - copper phthalocyanines.
- According to the invention, there is provided a process for production of a poly-chloro - polybromo - copper phthalocyanine which process comprises forming a melt of aluminum chloride, sodium bromide and optionally sodium chloride, introducing into said melt at a temperature of from 100°C to 170°C, a pulverulent mixture of copper phthalocyanine, aluminum chloride, sodium bromide and optionally sodium chloride, introducing chlorine into the melt simultaneously with introduction of the pulverulent mixture and, after the introduction of the pulverulent mixture has been completed, introducing chlorine into the melt at a temperature of from 90°C to 180°C.
- As will be appreciated from the Examples which follow, the process according to the invention gives polychloro - polybromo - copper phthalocyanines in high space-time yields and consistently high quality, the products having a high content of the pure pigment. The halogenation time required in the process according to the invention is, as will be appreciated from the Examples, 30 to 40% of the time required in the conventional processes.
- The process according to the invention may conveniently be carried out by initially introducing into the reaction vessel from 40 to 80% by weight of the total mixture of aluminum chloride, sodium bromide and, optionally, sodium chloride required for the halogenation, and fusing the mixture. With the melt at from 100 to 170°C, the mixture of copper phthalocyanine and the remaining aluminum chloride, sodium bromide and any sodium chloride is introduced whilst simultaneously passing in chlorine. When all the material has been introduced, chlorine is passed in at 90°C to 180°C until the desired ratio of chlorine to bromine is present in the reaction product. After reaching the end point, the reaction mixture is introduced into water to which hydrochloric acid has been added, whereupon the product precipitates; it is isolated by conventional methods.
- The ratio of aluminum chloride to sodium bromide is in general from 0.2 to 0.4 part by weight of sodium bromide per part by weight of aluminum chloride, so as to give a melt which can still be stirred easily at from 100 to 110°C. If appropriate, sodium chloride can also be added to the melt even before passing in chlorine.
- The quantities of the constituents which are used to form the melt depend on the desired ratio of chlorine to bromine in the products, the tinctorial properties of which can be varied systematically, for a degree of halogenation of from 14 to 16 halogen atoms per mole of copper phthalocyanine, by varying the ratio of chlorine atoms to bromine atoms in the compound. Thus, increasing the bromine content shifts the hue towards a more yellowish green.
- In general, the total combined amount of aluminum chloride, sodium bromide and optionally sodium chloride used is from 4 to 20 times, preferably from 6 to 10 times, the amount of copper phthalocyanine.
- Of the above amount, in general from 40 to 80% by weight, preferably from 60 to 70% by weight, is initially used to form the initial melt, usually by introducing the materials into a reaction vessel for the reaction and fusing them by heating. With the melt at from 110 to 170°C, preferably at from 110 to 140°C, the copper phthalocyanine is then introduced into the melt together with the remainder of the aluminum chloride and sodium bromide, in the form of a mixture. In general, this latter introduction of material requires from 1 to 3 hours.
- After introduction of the mixture of copper phthalocyanine, aluminum chloride, sodium bromide and optionally sodium chloride has been completed, chlorine simultaneously having been introduced, chlorine is introduced into the melt until the desired ratio of chlorine to bromine in the copper phthalocyanine has been reached. A preferred method is to pass chlorine into the melt, without attention to the ratio of chlorine to bromine in the halogenation product, until the off-gas shows substantial amounts of bromine vapour. In that case, the pigment obtained after working up is of particularly good quality and high content of pure pigment.
- On reaching the desired ratio of chlorine to bromine, the melt should preferably be introduced as rapidly as possible into water to which hydrochloric acid has been added; this precipitates the polychloro - bromo - copper phthalocyanine, enabling isolation of the product by conventional methods.
- Polychloro - polybromo - copper phthal-

cyanines can be manufactured in high space-time yields by the process of the invention. Thus a polychloro - bromo - copper phthalocyanine which contains about 13 bromine atoms can be manufactured in merely from 30 to 40% of the time required by the conventional processes. At the same time, the product according to the invention has a substantially increased content of pure pigment, namely more than 95% by weight as against from 85 to 95% by weight in products obtained by conventional processes. A further advantage of the polychloro - bromo - copper phthalocyanines obtained by the process according to the invention is that they lend themselves to all finishing processes and can be converted by these processes into high tinctorial strength pigmentary forms.

The Examples which follow illustrate further the process according to the invention. In the Examples, the parts and percentages are by weight.

#### Example 1

600 parts of  $\text{AlCl}_3$  and 240 parts of  $\text{NaBr}$  are mixed and fused at from 90 to 160°C. 15 parts of chlorine are passed in per hour and at the same time a pulverulent mixture of 400 parts of  $\text{AlCl}_3$ , 120 parts of  $\text{NaBr}$  and 130 parts of copper phthalocyanine is added at a temperature of from 100°C to 110°C in the course of from 1 to 3 hours, in approximately equal portions. As soon as the slight vapours of bromine have disappeared, the chlorine feed is increased to 30 parts per hour, the temperature is allowed to rise to as much as 160°C, and chlorine is passed in until pronounced vapours of bromine are formed. The reaction mixture is precipitated in a 10-fold amount of water, and worked up. 365 parts of crude pigment containing 8.6% of chlorine and 57% of bromine are obtained; this material can be finished, either in sulfuric acid or organic solvents, to give very valuable pigments.

The aluminum content of a sample which has been dried and reprecipitated from a 10-fold amount of sulfuric acid (see example 3c) is 0.09%; purity of the pigment: 97%.

#### Example 2

The procedure followed is as in Example 1, but before adding the mixture of copper phthalocyanine, aluminum chloride and sodium bromide and introducing chlorine, the temperature of the melt is adjusted to 120°C, and in the course of the reaction the temperature of the melt is allowed to rise to a maximum of 170°C.

After working up, 374 parts of a crude pigment containing 6.2% of chlorine and 61% of bromine are obtained. The crude pigment can be converted into valuable finished pigments by treatment with organic solvents. Purity of the pigment: 97%.

#### Example 3

(a) 600 parts of  $\text{AlCl}_3$ , 60 parts of  $\text{NaCl}$  and 130 parts of  $\text{NaBr}$  are mixed and fused at from 90 to 160°C. 15 parts of chlorine per hour are passed in and at the same time a pulverulent mixture of 400 parts of  $\text{AlCl}_3$ , 200 parts of a  $\text{NaBr}$  and 200 parts of copper phthalocyanine is added, at a temperature of from 100°C to 110°C, uniformly in the course of from 1 to 3 hours. As soon as the slight vapours of bromine which are formed initially have disappeared, the chlorine feed is increased to 30 parts per hour and chlorination is continued until pronounced bromine vapours are formed; during this stage, the temperature rises to 170°C. The reaction mixture is precipitated by introducing it into a 10-fold amount of water and is worked up by conventional methods. 486 parts of a crude pigment containing 22.2% of Cl and 39% of Br are obtained. The crude pigment can be finished either in sulfuric acid or in organic solvents, to give very valuable pigments. Purity of the pigment: 97%.

(b) A sample of the resulting crude pigment, which is moist with water, is finished for 3 hours at 100°C in accordance with Example 1 of German Patent No. 1,242,180, and is worked up by conventional methods.

A sample, moist with water, of the crude pigment obtained according to Example IV of British Patent Specification No. 925,266 is finished and worked up in the same way.

The resulting pigment powders are tested for their tinctorial properties, and compared with one another, in solvent-free stoving finishes at a specific depth of colour ( $1=1/9$  standard depth). For this purpose, a sample of each of the pigment powders is milled in Grinding Base S 100 (manufactured by Lawter Chemicals Inc., Chicago, U.S.A.) on a triple-roll mill. The colourations produced are evaluated in accordance with the FIAF programme, see Farbe und Lacke 75, 854—862 (1969), the hue and saturation of the colourations being measured according to DIN specification 6164. The tinctorial strength at 1/9 standard depth of colour according to DIN specification 53,235 is expressed, in accordance with the FIAF programme, in terms of the brightening ratio. The test results are summarized in the table which follows:

Example 3  
British Patent Specification No. 925,266  
Example IV

	BR	CE	H	S	D
	30.70	100	20.46	4.89	38
	24.42	125.5	20.49	4.91	23

5 CE=colour equivalent; H=hue; S=colour saturation; D=dispersibility; BR=brightening ratio

10 The dispersibility is a measure of the dispersibility of the pigment; higher figures denote easier dispersibility than lower figures.  
10 Accordingly, the pigment obtained by the process of the invention is 25.5 colour equivalents more economical in use or, expressed in percentage terms, of 22% greater tinctorial strength; it has practically 15 the same hue and the same colour saturation but its dispersibility, 38, indicates that it is almost twice as easily dispersible as the pigment of D 23 obtained by the conventional process.

(c) The purity of the pigments is determined as follows:

A dried sample of product (a) and a dried sample of the pigment obtained according to Example IV of British Patent Specification 925,266 are stirred for 16 hours at room temperature in 10-fold quantity of 96% strength sulfuric acid. The suspension is poured out into a 10-fold amount of water and the pigment is filtered off, washed neutral and free from salt and dried. Thereafter, the aluminum and copper contents of the samples are determined.

35 Example 3 (a)  
British Patent Specification No. 925,266  
Example IV

	% Al	% Cu	% Cu, calculated
	0.07	4.1	4.3
	0.58	3.0	4.3

wherein the weight ratio of aluminum chloride to sodium bromide is 1:0.2 to 1:0.4.

4. A process as claimed in any of claims 1 to 3, wherein a total of from 4 to 20 parts by weight of aluminum chloride and sodium bromide and, optionally, sodium chloride is used per part by weight of copper phthalocyanine.

5. A process as claimed in any of claims 1 to 3, wherein a total of from 6 to 10 parts by weight of aluminum chloride and sodium bromide and, optionally, sodium chloride is used per part by weight of copper phthalocyanine.

6. A process as claimed in any of claims 1 to 5, wherein from 40 to 80% by weight of the total amount of aluminum chloride, sodium bromide and, optionally, sodium chloride required is used to produce the initial melt.

7. A process as claimed in any of claims 1 to 5, wherein from 60 to 70% by weight of the total amount of aluminum chloride, sodium bromide and, optionally, sodium chloride required is used to produce the initial melt.

8. A process as claimed in any of claims 1 to 7, wherein chlorine is passed into the melt until pronounced vapours of bromine are evolved from the melt.

9. A process as claimed in any of claims 1 to 8, wherein the melt is introduced into

40 According to these results, the polychloro - bromo - copper phthalocyanine obtained by the conventional process contains 30% of polychloro - bromo - aluminum phthalocyanine. In contrast, the pigment obtained by the process of the invention contains less than 5% of aluminum polychloro - bromo - phthalocyanine.

#### WHAT WE CLAIM IS:—

1. A process for production of a polychloro - polybromo - copper phthalocyanine which process comprises forming a melt of 50 aluminum chloride, sodium bromide and optionally sodium chloride, introducing into said melt at a temperature of from 100°C to 170°C, a pulverulent mixture of copper phthalocyanine, aluminum chloride, sodium bromide and optionally sodium chloride, introducing chlorine into the melt simultaneously with introduction of the pulverulent mixture and, after the introduction of the pulverulent mixture has been completed, introducing chlorine into the melt at a temperature of from 90°C to 180°C.

2. A process as claimed in claim 1, wherein the mixture of copper phthalocyanine, aluminum chloride and sodium bromide is introduced at from 110 to 140°C.

65 3. A process as claimed in claim 1 or 2,

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water immediately after the end of the halogenation.

5 10. A process as claimed in any of claims 1 to 9, as described in any one of the Examples.

11. Polybromo - polychloro - copper phthalocyanine obtained by a process as claimed in any of claims 1 to 10.

J. Y. & G. W. JOHNSON,  
Furnival House,  
14-18 High Holborn,  
Chartered Patent Agents,  
London, WC1V 6DE.  
Agents for the Applicants.

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